

CHEMICALLY ENHANCED FOCUSED ION BEAM MICRO- MACHINING OF COPPER

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Related Applications

10 This application is a divisional of Application No. 10/284,784 filed October 31, 2002, assigned to the assignee of the present application, which is a divisional of Application No. 09/871,541, filed May 31, 2001, which application claims the benefit of United States provisional application serial number 60/261,109, filed January 12, 2001, the disclosures of which are hereby incorporated herein by reference in their entireties as if set forth fully herein.

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Field of the Invention

The present invention concerns the focused ion beam machining of copper on substrates such as microelectronic substrates.

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Background of the Invention

Focused ion beam machining (FIBM) is required for design debug, editing and verification, metrology, and process control of nanofabricated devices such as microelectronic substrates. *See, e.g.*, U.S. Pat. No. 5,188,705 to Swanson et al., U.S. Patent No. 6,140,655 to Russell et al., and U.S. Patent No. 5,798,529 to Wagner et al.

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Unfortunately, the current knowledge base associated with the FIBM of aluminum does not directly transfer to copper micro-machining. Copper is notoriously difficult to micro-machine uniformly with a focused ion beam since the micro-machining rate depends heavily on Cu grain orientation. J. Phillips et al., *J. Vac. Sci. Technol. A* **18**, 1061 (2000); D. Thaus et al., *J. Vac. Sci. Technol. B* **14**, 3928 (1996). Accordingly, there is a need for new ways to carry out the focused ion beam, or other particle beam, machining of copper.

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Summary of the Invention

5 A first aspect of the present invention is, accordingly, a method of micromachining a copper layer on a substrate. The method comprises: bombarding a portion of the substrate (particularly the copper layer) with a particle beam (*e.g.*, a focused beam or charged particle beam) from a particle source; and exposing the substrate to a supply of organic chloride or organic hydroxide during particle bombardment, the organic chloride or organic hydroxide vapor concentration at the
10 substrate being sufficient to enhance removal (including removal in whole or removal in part) of the copper layer. The substrate is preferably maintained in a vacuum during the bombarding and exposing steps. The vacuum need only be sufficient for achieving the intended purpose of micromachining the copper, and need not be absolute.

15 A second aspect of the present invention is a method of selectively removing a first, copper material from a substrate to expose a neighboring (underlying or adjacent) layer of a second material. The method comprises maintaining the substrate in a vacuum; bombarding with a particle beam (*e.g.*, a focused beam or charged particle beam) a portion of the substrate having a first copper material neighboring a
20 second material such as a dielectric; and exposing the portion of the substrate to an organic chloride or organic hydroxide during particle bombardment of the substrate, the first copper layer having a sputter etch rate that either 1) is increased by the presence of organic chloride or organic hydroxide vapor and the second material having a sputter etch rate that is not increased by the presence of organic chloride or
25 organic hydroxide vapor to the degree that the sputter etch rate of the first material is increased, thereby selectively sputtering the first material compared with the second material; or is decreased by the presence of organic chloride or organic hydroxide vapor and the second material having a sputter etch rate that is decreased by the presence of organic chloride or organic hydroxide vapor to the degree that the sputter
30 etch rate of the second material is decreased, thereby selectively sputtering the first material compared with the second material; or a combination of both. In one

embodiment, the second material underlies the first material. In a particular embodiment, exposing the substrate to a supply of organic chloride or organic hydroxide includes exposing the substrate to organic chloride or organic hydroxide vapor at a partial pressure of approximately 1 mTorr. In one preferred embodiment, the particle beam comprises a beam of gallium ions focused to a sub-micron target point.

A further aspect of the present invention is a method of shaping features of a surface of a solid object having a surface. The method comprises the steps of: positioning the object within an enclosed chamber; supplying organic chloride or organic hydroxide vapor within the chamber so that organic chloride or organic hydroxide is adsorbed onto the exposed surface of the object for enabling a chemical reaction between the organic chloride or organic hydroxide and a copper layer at the surface; generating a particle beam (*e.g.*, a focused beam or charged particle beam); and directing the beam toward the surface for removal by sputtering of a portion of the copper layer, the particle-beam induced chemical reaction between the organic chloride or hydroxide and the copper layer increasing the sputtering selectivity of the copper layer relative to the neighboring layer and especially the underlying layer.

A still further aspect of the present invention is a method of chemically-enhanced particle beam machining of a copper layer on a substrate for cross-sectional analysis. The method comprises maintaining a substrate in a vacuum; applying an organic chloride or organic hydroxide to the substrate; and bombarding with a particle beam (*e.g.*, a focused beam or charged particle beam) a portion of the substrate including thereon a copper layer to expose for examination a cross section of the copper layer. The organic chloride or organic hydroxide is applied to the substrate at a concentration sufficient to enhance removal of the copper layer.

Still further aspects of the present invention include the products which may be produced by the processes described herein.

The present invention also provides a focused particle beam metrology device. The device comprises: a particle beam (*e.g.*, a focused particle beam or charged particle beam) source which produces low intensity focused particle beams directed to a semiconductor device having features thereon; a detector which detects electrons or

ions emitted from the semiconductor device; a processor which receives data from the detector and measures dimensions of the features from the data; a discharge device which introduces an organic chloride or organic hydroxide toward the semiconductor device (the device preferably including a copper layer as described herein); and a control device connected to the particle beam device to vary intensity of the focused particle beams for generating high intensity focused particle beams to etch the semiconductor device. Preferably the detector is located substantially above the semiconductor device for top-down linewidth measurements. The device may include a display device connected to the processor, wherein the display device displays an image of the semiconductor device. The high intensity focused particle beams may partly or completely etch through the semiconductor device. In one embodiment, the high intensity particle beams etch a crater in the semiconductor device exposing a cross-section of the semiconductor device, and the low intensity particle beams scan the cross-section at a predetermined angle to form an image of the cross-section. The device may further include a movable platform for holding the semiconductor device, wherein the movable platform is tilted at the predetermined angle during the low intensity particle beam scanning of the cross-section.

In a particular embodiment of the foregoing, the present invention provides a method of forming a three dimensional profile of a copper feature of a semiconductor device, the method comprising the steps of: introducing an organic chloride or organic hydroxide toward the semiconductor device through a discharge device; etching a top surface of the feature with a high intensity focused particle beam from an particle beam source; forming a top-down image of the top surface on an image forming device connected to a processor; repeating the etching and forming steps until the feature is completely etched from top to bottom to form successive top-down images of the etched feature; and overlaying the top-down images of the feature by the processor to form the three dimensional profile of the feature.

In another particular embodiment of the foregoing, the present invention provides a method of measuring a cross-section profile of a copper layer of a semiconductor device which comprises the steps of: introducing an organic chloride or organic hydroxide toward the semiconductor device through a discharge device;

etching a crater to expose the cross-section by a high intensity focused particle beam generated from a first particle beam source; directing a low intensity particle beam toward the cross-section; and forming an image of the cross-section on an image forming device from low intensity particle beams generated from the particle beam source and reflected from the cross-section.

The foregoing and other objects and aspects of the present invention are explained in greater detail in the drawings herein and the specification set forth below.

Brief Description of the Drawings

Figure 1 is a schematic representation of a focused ion beam system adapted for carrying out the process of the present invention.

Figure 2 is a schematic illustration of the gas injection system for providing organic chloride or organic hydroxide vapor.

Figure 3 shows an SEM micrograph, taken at 30 degrees tilt, of unassisted FIB machined copper with 25keV Ga^+ , 0.5 nA, 130 nm spot size; 50% beam overlap, 0.1usec dwell time showing large induced topography.

Figure 4 shows an SEM micrograph, taken at 30 degree tilt, of $\text{C}_2\text{H}_4\text{Cl}_2$ chemical assisted FIB machined copper with 25keV Ga^+ , 0.5 nA, 130 nm spot size; 50% beam overlap, 0.1 usec dwell time showing very small waving topography and reduced redeposition.

Figure 5 shows an SEM micrograph, taken at 20 degree tilt, of C_2Cl_4 , chemical assisted FIB machined copper with 25 keV Ga^+ , 0.5 nA, 130 nm spot size; 50% beam overlap, and 0.1 usec dwell time, showing reduced topography and redeposition.

Figure 6 shows SE vs. FIBM (0 to 9 min. 10 sec) obtained during FIBM of the crater in Figure 5. SE emission stabilizes after removal of the copper. The copper layer is completely removed after 4 min, 35 sec.

Figure 7 shows a comparison between SiO_2 sputtering rates with some of the chemistries covered by this patent and one not— H_2O , and indicating ethanol as being currently preferred.

Detailed Description of the Preferred Embodiments

The present invention is described more fully hereinafter with reference to the accompanying drawings, in which preferred embodiments of the invention are shown.

5 This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. In the drawings, the thickness of layers and regions may be exaggerated for clarity.

10 Focused particle beam machining is known and disclosed, for example, in U.S. Pat. No. 5,188,505 to Swanson et al., U.S. Patent No. 6,140,655 to Russell et al., and U.S. Patent No. 5,798,529 to Wagner et al., the disclosures of which are incorporated herein by reference. Any type of particle beam can be used, including electron beams and ion beams, with ion beams such as gallium ion beams being
15 currently preferred.

“Organic hydroxide” as used herein refers to any carbon compound (that is, a compound with a carbon backbone) that contains one or more hydroxide radicals, including but not limited to C1 to C4, C6, or C8 (or more) compounds. “Organic chloride” as used herein refers to any carbon compound (that is, a compound with a
20 carbon backbone) that is substituted one or more times with a chlorine atom, including but not limited to C1 to C4, C6, or C8 (or more) compounds. (The term “organic chloride” also includes compounds containing both chlorine and a hydroxide radical.) The organic chloride or organic hydroxide compounds may be linear or branched and saturated or unsaturated (e.g., containing one, two or more double
25 bonds). The carbon backbone may also be substituted with one or more additional atoms such as hydrogen, or may be completely substituted with chloride and or organic hydroxide groups. The carbon backbone may consist entirely of carbon, but may optionally contain hetero atoms such as nitrogen, oxygen and/or sulfur. Preferably the organic chloride or organic hydroxide is one that may be introduced
30 into the vacuum as a vapor. In a preferred embodiment, the organic chloride is $C_xH_yCl_z$, where x is 1 or 2 to 4, 6 or 8; y may be 0; z is at least 1 or 2; and the total of

- 7 -

y and z is dependent upon the number of substituents available for the compound based upon x and the degree of branching and unsaturation of the carbon atoms in the molecule. Specific examples include, but are not limited to:

- 5 $C_2H_4Cl_2$ (dichloroethane),
- C_2Cl_4 (tetrachloroethene),
- CCl_4 (tetrachloromethane or carbon tetrachloride),
- $CHCl_3$ (trichloromethane or chloroform),
- CH_2Cl_2 (dichloromethane),
- C_2Cl_4 (tetrachloroethene),
- 10 C_2Cl_6 (hexachloroethane),
- C_2HCl_3 (trichlorethene),
- C_2HCl_5 (pentachloroethane),
- $C_2H_2Cl_2$ (cis 1,2 Dichloroethene),
- $C_2H_2Cl_2$ (1,1 dichloroethene),
- 15 $C_2H_4Cl_2$ (1,2 dichlorethane),
- $C_2H_2Cl_4$ (1,1,2,2 tetrachloroethane),
- $C_2H_2Cl_4$ (1,1,1,2 tetrachlorethane),
- $C_2H_3Cl_3$ (1,1,1 trichloroethane),
- $C_2H_3Cl_3$ (1,1,2 trichlorethane).

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In a preferred embodiment, the organic hydroxide is $C_xH_y(OH)_z$ where x is 1 or 2 to 4, 6 or 8; y may be 0; z is at least 1 or 2; and the total of y and z is dependent upon the number of substituents available for the compound based upon x and the degree of branching and unsaturation of the carbon atoms in the molecule. Specific

25 examples include, but are not limited to:

- C_2H_5OH (ethanol),
- $C_2H_4(OH)_2$ (dihydroxyethane),
- $C_2H_3(OH)_3$ (trihydroxyethane),
- 30 $C_2H_2(OH)_4$ (tetrahydroxymethane),
- $C_2H(OH)_5$ (pentahydroxymethane)

- 8 -

C₂H(OH)₃ (trihydroxyethene),
CH₃OH (methanol),
CH₂(OH)₂ (dihydroxymethane),
CH(OH)₃ (trihydroxymethane), and
5 C(OH)₄ (tetrahydroxymethane).

Examination of the literature has found that hydroxide radicals have been reported to enhance the removal of copper during mechanical polishing (M Hariharaputhiran et al., **J. Electrochem. Soc.** **147** (2000) 3820). The production of
10 these during wet-chemistry, mechanical polishing requires the addition of an amino-acid to the slurry. This in no means indicates that the use of organic hydroxides would enhance the removal of copper during the dry-chemistry process of FIBM would enhance the relative etching of copper over SiO₂.

“Copper” as used herein refers to any type of copper material, including
15 copper alloys, employed in semiconductor fabrication. The copper may be in or on any type of substrate, such as a semiconductor substrate or device. The copper layer may overlie a second material, typically a dielectric. Examples of dielectric materials include, but are not limited to, SiO₂, SiN, SiON, ON, ONO, BPSG, PSG, USG, etc. The copper layer may have a thin overlying or underlying layer between the copper
20 layer and the underlying substrate or dielectric, such as a thin diffusion barrier, passivated layer, oxide layer or insulating layer. Examples of copper layers and substrates that may be the workpiece in the present invention include, but are not limited to, that shown in U.S. Patents Nos. 6,057,223; 5,959,358; 5,899,740; and 5,766,379, the disclosures of which are incorporated by reference herein in their
25 entirety.

Referring to **Figure 1**, a focused particle beam system for selectively increasing the rate of removal of certain materials and decreasing (or relatively decreasing) the rate of removal of other materials according to the present invention is illustrated. An evacuated envelope **10** includes an upper neck portion **12** within which
30 a liquid metal ion source **14** and a focusing column **16** are located. The particle beam **18** passes from the source **14** through the column **16** and between electrostatic

deflectors **20** toward substrate or workpiece **22**, which is positioned on a movable X-Y stage **24** within the lower chamber **26**. The workpiece **22** can be any device or substance capable of being machined by a charged particle beam, including, but not limited to, microelectronic devices including semiconductors, optical devices, and any
5 device having multi-layer coatings. An ion pump **28** is employed for evacuating the neck portion **12**. The lower chamber **26** is evacuated with a pumping system **30** operated by a vacuum controller **32**.

A high voltage power supply **34** is connected to the liquid metal ion source **14** as well as to electrodes (not shown) contained within the focusing column **16** for
10 forming an approximately 25 keV particle beam **18** and directing the beam downwardly in the direction of the workpiece **22**. The deflection controller and amplifier **36**, which is operated in accordance with a prescribed pattern such as a raster pattern provided by the pattern generator **38**, is coupled to the electrostatic deflection means **20**, whereby the particle beam **18** can be controlled to sputter a
15 pattern on the upper surface of the workpiece **22**. In one embodiment, the liquid metal ion source **14** provides a beam of gallium ions, although other ions or particles could be used. In another embodiment, the particle beam **18** could comprise electrons.

For metrology applications and other detection steps, the device may also include a detector **60** operatively associated with a computer **61** or other processor, as
20 well as a drive **70** for tilting the X-Y stage. The detector is located above the sample as noted previously. Computer **61** may be operatively associated with an imaging or display device **62** for displaying an image of the sample, or the image may simply be stored for future display. All may be implemented and or configured for measuring dimensions of the sample, as described in U.S. Patent No. 5,798,529 to Wagner et al.
25 (the disclosure of which is incorporated by reference herein in its entirety) with the addition of a organic chloride or organic hydroxide source as described herein.

In accordance with the present invention, the focused particle beam system of **Figure 1** is further provided with a source **46** for supplying organic chloride or organic hydroxide. The organic chloride or organic hydroxide may be provided in
30 any suitable manner, preferably as a vapor. In a preferred embodiment, the organic chloride or organic hydroxide vapor is provided via a gas injection system,

schematically illustrated in **Figure 2**, and comprises a liquid reservoir **49** for the organic chloride or organic hydroxide, injection needle **50**, leak valve **47**, and shut-off valves **51**. The organic chloride or organic hydroxide vapor is fed to the surface of the substrate or workpiece **22** through an injection needle **50** that is preferably
5 positionable to within approximately 100 μm of the workpiece. The gas flow from the organic chloride or organic hydroxide vapor source **46** may be controlled, for example, using a variable leak valve **47**, such as a Granville Phillips Series 203 valve, as would be known to those skilled in the art. Also, as would be known to those skilled in the art, the gas pressure at the entrance to the injector needle **50** may be
10 monitored using a suitable vacuum gauge **48**. For example, for a 0.5 mm outside diameter needle, a desirable flow rate through the needle would be approximately 2×10^{-6} torr-liter/sec, yielding a pressure at the workpiece surface of approximately 1 mTorr, although, as would be understood by those having skill in the art, other flow rates and pressures at the surface of the workpiece **22** would be acceptable.

15 The present invention is useful, among other things, for design debug, editing and verification; metrology, and process control of microfabricated devices or substrates such as semiconductor substrates. In one embodiment, the present invention enhances the relative selectivity of removal of the copper material as compared to neighboring, adjacent or underlying second materials, such as an underlying
20 dielectric. Thus, in one embodiment, the present invention provides the capability to stop etching at the interface (*e.g.*, substantially precisely at the interface) between a copper layer and a second material (*e.g.*, a dielectric) in a substrate. The present invention may provide for high resistance trace cutting for editing. In another embodiment, the present invention may provide for the substantial absence or
25 reduction of re-deposition of residue from the etching process that spontaneously reacts upon exposure to air/water vapor.

The advantages of the present invention will be apparent from the information shown in **Figures 3-7**. Sputter induced roughness/topography, resulting from unassisted Focused Ion Beam Micromachining (FIBM) of $5 \times 5 \mu\text{m}^2$ areas of a copper
30 film, was found to be as as high as 50% for a sputtered copper depth of 2 μm , typical of IC top metallization (see **Figure 3**). This FIBM induced roughness resulted in an

inability to completely clear copper in the micromachined areas without removing large amounts of dielectric. Thus stopping at the copper-barrier layer/dielectric interface as well as end point detection, by whatever means, was impossible. With $C_2H_4Cl_2$, chemically enhanced FIBM (CE-FIBM) increased the FIBM selectivity (defined as the material removal rate, in this case, of copper versus that of dielectric) between copper and dielectric and reduced the FIBM induced topography (see **Figure 4**), but some topography was created. The use of C_2Cl_4 for CE-FIBM of copper resulted in a small increase in copper material removal rate (about $0.5 \text{ } \mu\text{m}^3/\text{nC}$) and a significant reduction of FIBM induced topography at the copper-barrier layer/dielectric interface (see **Figure 5**), providing a dramatic improvement in endpoint detection. (see **Figure 6**). The improved ability to detect the endpoint by SE emission results from an increase in copper versus dielectric FIBM selectivity. The improvement in relative etch rates depends on both the enhancement of the copper etch rate as well as the retardation of the dielectric etch rate. Certainly the retardation is an important consideration (see **Figure 7**). From voltage contrast imaging, the resistivity of a cut seems to meet what is required for trace cutting during editing operations. Further, after two weeks of exposure of the $C_2H_4Cl_2$ the C_2Cl_4 and the C_2H_5OH CE-FIBM samples to "laboratory" air (about 30% humidity), no observable corrosion or reaction products were found.

In the drawings and specification, there have been disclosed typical preferred embodiments of the invention and, although specific terms are employed, they are used in a generic and descriptive sense only and not for purposes of limitation, the scope of the invention being set forth in the following claims.